ADDENDUM

GWERD QUALITY ASSURANCE PROJECT PLAN

TITLE: Ground-Water Investigation in Pavillion, Wyoming

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Purpose

The purpose of this Addendum to the QAPP for the *Ground-Water Investigation in Pavillion, Wyoming, Revision No. 6,* is to describe the following changes and their applicability to the project:

Part 1 – Definitions of Data Qualifiers.
Applicability: All analyses in the entire data set.

Part 2 – Description of the application of data qualifiers to samples effected by potential contamination in associated Lab Blanks, Trip Blanks, Field Blanks, and Equipment Blanks.
Applicability: All analyses in the entire data set.

Part 3 - Description of the time series sampling of MW01.
Applicability: Only the time series sampling of MW01.

Part 4 - Description of changes to the sampling scheme for Field and Equipment blanks.
Applicability: Field sampling.

Part 5 - Specifications for the reanalysis of samples for trace metals by ICP-MS.
Applicability: Only the reanalysis for trace metals by ICP-MS.

Part 6 - Region 8 Laboratory VOC Preservation: TSP vs. HCl issue.
Applicability: VOC analysis by Region 8 Laboratory

Part 7 - Revision of QC criteria for metals analysis by ICP-OES
Applicability: Shaw Environmental ICP-OES analysis of metals

Part 1

The following data qualifiers are to be applied to all project data sets.

Table 1. Data Qualifiers

Qualifier	Definition
U	The analyte was analyzed for but not detected above the reported method detection limit (MDL). Results are displayed as <MDL value.
U1	The analyte was analyzed for but not detected above the reported quantitation limit (QL). Results are displayed as <QL value.
LB	The analyte is found in an associated laboratory blank above QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
TB	The analyte is found in an associated trip blank above QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
FB	The analyte is found in an associated field blank above QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
EB	The analyte is found in an associated equipment blank above QL and the concentration found in the sample is less than 10 times the concentration found in the blank.
D(value)	The reported value is from a dilution. (Value) is equal to the dilution factor.
R	The data are unusable. The sample results are rejected due to serious deficiencies in the ability to analyze the sample and/or meet quality control criteria.
K1	Samples may be biased high because of high % recoveries in some LCS and/or MS/MSD samples.
K2	Samples may be biased low because of low % recoveries in some LCS and/or MS/MSD samples.
K3	Potential spectral (mass or emission) interference.
J0	Estimated value. Results displayed are above method detection limit (MDL) and below quantitation limit (QL).
J1	Estimated value. Laboratory calibration criteria not met.
J2	Estimated value. Laboratory QA/QC acceptance criteria not met.
J3	Sample bottles received from the field were damaged.
J4	Problem with sample extraction.
J5	Holding time exceeded.
J6	Laboratory duplicate not within control limits.
J7	Field duplicate not within control limits.

J8	Estimated value. Screening data.
J9	Sample not properly preserved.
T	Tentatively Identified Compound (TIC)
NA	Data not reported or collected.
	If the analyte concentration is <QL, then the qualifiers LB, TB, FB, or EB were not applied.
	For samples associated with high MS recoveries, the K1 qualifier is not applied if the analyte is <QL
	For samples associated with low MS recoveries, the K2 qualifier is applied regardless of analyte concentration (< or > QL)

Part 2

Application of Data Qualifiers

The QAPP, Revision No. 6, in Section 6.3 states that, "Analytes detected in various blank samples will be evaluated and flagged in presentations of data. Generally, blank contamination will be considered to be significant when blank contaminants are found at a level within 3 times that found in applicable field samples." This approach is revised to the following: "Analytes detected in various blank samples will be evaluated and flagged based on the following criteria. Blank contamination will be considered significant when blank contaminants are found above the QL (Quantitation Limit) and the concentration found in the associated sample is less than 10 times the concentration found in the blank." Samples assigned a numeric value in the range greater than the method detection limit but less than quantitation limit will be qualified as estimated with a J0 qualifier. See Table 1 for the list of Data Qualifiers used to flag samples with QC (Quality Control) issues that were identified during data review and validation.

Part 3

Time Series Sampling of MW01

An important addition was made to the sampling approach for MW01 following the preparation and approval of version 6 of the QAPP. This addition was documented in an email (4/12/2012) from a co-PI to the QA Manager overseeing this project. The email text is provided below. The following is a change to the sampling strategy for MW01. The sampling methodology below supersedes the presentation in the QAPP titled "Ground-Water Investigation in Pavillion, Wyoming" (v6, 2/17/2012, QA ID NO. G-14478).

The USGS-EPA technical workgroup, upon consensus agreement, determined that samples were to be collected at MW01 after attainment of stabilization parameters and after purging one borehole volume. Subsequently, a letter from WYDEQ to USGS provided direction for USGS to

additionally remove three casing (now borehole, based on current USGS Sampling and Analysis Plan) volumes prior to sampling at MW01. Thus, two sample collection events, at 1 and 3 borehole volumes, respectively, are currently planned. There should be no expectation that the exact same concentration of various analytes will be observed at both sampling points due to laboratory variability and oscillatory behavior frequently observed in published studies on time series testing during purging. When there is oscillatory behavior, two samples cannot define a trend. Also purge volume may impact observed sample concentrations. Consequently, it is necessary for EPA to conduct a time-series analysis at MW01 to fully characterize expected variability in concentration during purging. Time-series analysis typically involves collection of at least 10 samples over time.

The following approach will be followed by EPA during the April 2012 sampling of MW01.

1) A sample will be collected after purging 1 borehole volume (approx. 410 gallons) and after stabilization of field parameters. This is similar to the approach used during the Phase IV sampling event and the approach was agreed on by the USGS-EPA technical workgroup. This sample will be collected in duplicate (labeled EPAMW01-0412 and EPAMW01d-0412).

2) Samples will be collected after approx. every 90 gallons of continuous purging for dissolved metals (filtered), anions (filtered), water isotopes (filtered), RSKSOP259 (alcohols and volatile organics), and GRO. An identical sampling approach will be utilized as described in the QAPPv6 (same bottles, preservation, storage). Sequential samples will be labeled with -x, e.g., EPAMW01-0412-2 or EPAMW01-0412-5, for the second and fifth sample collected in series, respectively. This series of samples is intended to provide reasonable time-dependent data for major and minor elements as well as organic compounds of interest (e.g., GRO and isopropanol). The water isotope data will useful in evaluating whether significantly different water sources are pulled into the screened during interval during the prolonged purging.

3) After approximately every 270 gallons, in addition to the samples noted in 2) above, samples for glycols, MBAS, ethoxylated compounds, DRO, and SVOCs will be collected for analysis. Again see QAPPv6 for sample collection details. These samples are needed to track time-dependent (volume-dependent) behavior of critical organic analytes.

4) Finally after approx. 3 borehole volumes and stabilization of parameters, a final complete sample set will be collected. This sample will be labeled EPAMW01-0412-10.

After each sample is collected, the time will noted and water volume pumped will be noted in order to correlate the sampling point with geochemical parameters recorded in the purge log and recorded water levels in the well.

Part 4

Collection of Field and Equipment Blanks

During field sampling a deviation occurred from the guidelines discussed in the QAPP. The

QAPP stated that field and equipment blanks would be collected on each day of sampling. Sampling occurred on seven days from April 16 to April 24. Collecting blanks on each sampling day would have resulted in an unnecessarily large number of field and equipment blank samples submitted for analysis, and would have amounted to almost one field and equipment blank per location where a complete sample set was collected (7 field/equipment blank samples to 10 complete sample sets). Consequently, field blanks were collected on the 16th, 18th, 22nd, and 24th of April. Samples collected on April 17th (PGDW23 and PGDW30) were evaluated for blank contamination using blank samples from April 16th. Samples collected on April 19 and April 20 (PGDW20 and PGPW02) were evaluated for blank contamination using blank samples from April 18th. Importantly, field and equipment blanks were collected on each occasion that MW01 and MW02 were sampled. Also, Trip Blanks were included in every sample shipment back to the analytical laboratories in accordance with the QAPP guidelines.

Part 5

Reanalysis of samples for trace metals by ICP-MS

Purpose

The purpose of this part of the QAPP addendum is to provide specifications and quality control (QC) acceptance criteria for the reanalysis of samples for trace metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Analysis of the original ICP-MS results for Phase V found that the laboratory did not analyze interference check solutions (ICSs) as described in EPA Method 6020A. These ICSs would have enabled the laboratory to evaluate the analytical method's ability to appropriately handle known potential interferents and other matrix effects. In ICP-MS analysis, the ICS is used to verify that the interference levels are corrected by the data system within quality control limits. Because of the importance of this missing quality control check, it was necessary to reject the data from the original analysis.

Five of the analytes (As, Cr, Cu, Ni, and Se) were reanalyzed at the same laboratory, with appropriate ICS QC checks. Other metals were not reanalyzed at the same time because the original analyses indicated concentration levels that were below the method quantitation level (e.g., Hg, Cd, Th) or because there are no relevant spectral interferences to correct (e.g., Pb, Sb, U, Tl). Notwithstanding, it was deemed appropriate to obtain a separate data set in a timely manner. The samples will be analyzed through the EPA Superfund Analytical Services Contract Laboratory Program (EPA CLP). Samples will be sent for analysis under the EPA CLP Inorganic Statement of Work ISMO1.3, Exhibit D – Part B, "Analytical Methods for Inductively Coupled Plasma – Mass Spectrometry" (http://www.epa.gov/superfund/programs/clp/ism1.htm#pdf), with some minor requested modifications described in the Analytical Methods section below.

Sample Handling and Custody

Samples will be packed in coolers (without ice) and shipped overnight via UPS or Fedex, to the contract laboratory awarded the work through the CLP, with appropriate chain of custody forms (see Figure 8) and the cooler will be sealed with custody seals.

Sample receipt and log-in shall be conducted as described in EPA CLP Inorganic Statement of Work ISMO1.3, Exhibit F – "Chain-of-Custody, Document Control, and Written Standard Operating Procedures" (http://www.epa.gov/superfund/programs/clp/download/ism/ism12e-h.pdf).

Analytical Methods

The contract laboratory shall analyze water/aqueous samples for Cd, Cr, As, Cu, Pb, Ni, Se, Tl and Sb by ICP-MS. The reanalysis will not include Hg, Th, or U. Mercury is excluded because the sample holding time is exceeded. Th and U are excluded because the specialized low-level quantitation request for these elements cannot be accommodated in the necessary timeframe. The contract laboratory shall perform the analysis in accordance with the EPA CLP Inorganic Statement of Work (SOW) ISM01.3, Exhibit D – Part B, "Analytical Methods for Inductively Coupled Plasma – Mass Spectrometry" (http://www.epa.gov/superfund/programs/clp/ism1.htm#pdf), with the following modifications:

[Note that for analysis conducted under the EPA CLP SOW, samples are grouped into batches of up to 20 called Sample Delivery Groups (SDGs).]

The contract Laboratory shall analyze water/aqueous samples for the Target Analyte List (TAL) (Cd, Cr, As, Cu, Pb, Ni, Se, Tl and Sb) by ICP-MS as indicated on the Traffic Report/Chain of Custody Record and Laboratory Scheduling Notification form.

Some samples may be received at a reduced volume, less than 100 ml but greater than 50 ml. The samples will not be shipped at 4°C (±2°C). The Laboratory shall note the temperature at the time of receipt in the SDG Narrative and proceed with analysis.

The Laboratory shall perform the Initial Calibration as currently in the SOW except that the lowest non-blank standard be set at the CRQL for all analytes.

The acceptance criterion for the initial calibration correlation coefficient is modified to $r \geq 0.998$.

The Laboratory shall re-analyze the low-level (at CRQL) calibration standard at the end of the run. The Percent Difference between the true value and the measured value shall be within ±30%.

The CCV and CCB shall be analyzed after every 10 analytical samples.

As part of the complete data package, the Laboratory shall provide:

- All masses monitored, and all masses used for quantitation.
- All corrections applied to the data to handle interferences and used to generate the final corrected instrument result.

Quality Control

The following Table 2 summarizes the acceptance criteria and frequency for the QC checks conducted during the course of sample analysis.

Table 2. CLP QC Checks for ICP-MS

QC Type or Operation	Acceptance Criterion	Frequency
Instrument Calibration	The acceptance criterion for the initial calibration correlation coefficient is r ≥0.998.	Each time instrument is turned on or set up, after ICV or CCV failure, and after major instrument adjustment. The lowest non-blank standard shall be set at the CRQL for all analytes.
Initial Calibration Verification	90-110% Recovery; % RSD≤5% for all replicate integrations	Following each instrument calibration for each mass used.
Initial Calibration Blank	≤CRQL	Following each instrument calibration, immediately after the ICV.
Continuing Calibration Verification	90-110% Recovery; % RSD≤5% for all replicate integrations;	For each mass used, at a frequency of at least after every 10 analytical runs, at the beginning of each day, and at the beginning and end of each run.
Low Level (at CRQL) Calibration Verification	70-130% Recovery	The Laboratory shall re-analyze the low-level (at CRQL) calibration standard at the end of each run.
Continuing Calibration Blank	≤CRQL	At a frequency of at least after every 10 analytical runs, at the beginning of each day, and at the beginning and end of each run. Performed immediately after the last CCV.
Interference Check Sample	±20% of the analyte's true value or ±2 times the CRQL of the analyte's true value, whichever is greater.	At the beginning of the run after the ICB but before the CCV.

Serial Dilution for ICP	If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	For each matrix type or for each SDG, whichever is more frequent.
Preparation Blank	≤CRQL	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Laboratory Control Sample	70-130% Recovery	For each SDG or each sample preparation and analysis procedure per batch of prepared samples, whichever is more frequent.
Spike Sample	75-125% Recovery	For each matrix type or for each SDG, whichever is more frequent.
Post-Digestion Spike	75-125% Recovery	Each time Spike Sample Recovery is outside QC limits.
Duplicate Sample Analysis	RPD<20 for sample values ≥5x CRQL; for sample values <5xCRQL, control limit = CRQL	For each matrix type or for each SDG, whichever is more frequent.
ICP-MS Tune	Mass calibration must be within 0.1 amu over the range of 6 to 210 amu, or the percent Relative Standard Deviation (%RSD) of all the integrations of the absolute signals of the analytes must be ≤5.0%.	Prior to calibration.
Internal Standards	The absolute response of any one internal standard must not deviate more than 60-125% from the original response in the calibration blank.	Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels.

Determination of Method Detection Limits		Prior to contract award, annually thereafter, and after major instrument adjustment.

Data Review and Validation

Initial data validation shall be conducted by the EPA CLP Sample Management Office (SMO) contractor. The EPA CLP SMO contractor shall perform a data assessment on the laboratory's hardcopy and electronic deliverable based on the requirements of the EPA CLP SOW ISMO1.3, the elements of the modified analysis as described above (and in the Request for Proposal),and the "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (http://www.epa.gov/superfund/programs/clp/download/ism/ism1nfg.pdf).

Quality Assurance Managers (QAMs) in NRMRL will subsequently conduct an Audit of Data Quality on the data set according to NRMRL SOP LSAS-QA-02-0 "Performing Audits of Data Quality (ADQs)". QAMs will review the information presented in the EPA CLP SMO data assessment, review the data, check the transcription of numbers from the lab reports into the Pavillion data tables, and ensure that appropriate project-specific data qualifiers were added to the Pavillion data tables.

Reporting Requirements

Hardcopy and electronic data reporting are required as specified per EPA CLP SOW ISM01.3. All hardcopy and electronic data shall be adjusted to incorporate modified specifications. This includes attaching a copy of the requirements for modified analysis to the SDG Narrative. All samples analyzed for the same fraction within an SDG must be analyzed under the same fractional requirements. The Laboratory shall not include data for the same fraction with different requirements in the same SDG.

The Laboratory shall include the Modification Reference Number on each hardcopy data form under the "Mod. Ref. No:" header appearing on each form as well as the SamplePlusMethod/ClientMethodModificationID element of the electronic deliverable. The Laboratory shall also document the Modification Reference Number and Solicitation Number on the SDG Coversheet and SDG Narrative.

Part 6

Region 8 Laboratory VOC Preservation: TSP vs. HCl issue

Prior to sampling a change was made in the preservative to be used for VOC samples to be analyzed by the Region 8 Laboratory. As presented in the QAPP, v6, trisodium phosphate (TSP) was to be used as the preservative. Normally the R8 laboratory used HCl. After the Region 8 laboratory determined that one or more analytes would be affected by base hydrolysis, and that all of their calibration and QC is based on the HCl preservative, the preservative was changed to HCl.

Part 7

Revision of QC criteria for metals analysis by ICP-OES

As a result of ADQs (Audits of Data Quality) it brought to light the need to re-examine the QC criteria for metals analysis by ICP-OES. In general, the QC criteria in the QAPP, v6, provides for spikes and duplicates to evaluate precision and accuracy for 80% of the metals (see Table 3 in QAPP, v6). Individual results with much greater or lesser recoveries may not be apparent using this criteria. The metals QC criteria were revised as presented in Table 3 to evaluate precision and accuracy for every metal.

Table 3. Revised QC Criteria for Metals analyzed by ICP-OES

Measurement	Analysis Method	Blanks (Frequency)	Calibration Checks (Frequency)	Second Source (Frequency)	Duplicates (Frequency)	Matrix Spikes (Frequency)
Metals (undigested, dissolved)	RSKSOP-213v4	<QL (Beginning and end of each sample queue & every 10 samples)	90-110% of known value (Beginning and end of each sample queue & every 10 samples)	PE sample acceptance limits; or other than PE, 90-110% of known value (Immediately after first calibration check)	RPD≤15 for metals ≥5x QL (Every 10 samples)	80-120% Rec. (one per 20 samples)
Metals (digested, total)	RSKSOP-213v4	<QL (Beginning and end of each sample queue & every 10 samples) Digestion blank (Every 20	See "undigested"	See "undigested"	RPD≤20 for metals ≥5x QL (Every 20 samples)	Pre-digestion: 75-125% Rec. (one per 20 samples); post-digestion: analyzed if pre- exceeds limits, same limits as pre-

		samples)				;LCS has same limits and frequency